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(54) Title of Invention: **Textile Treatment Agent**

## SPECIFICATION

### 1. Title of the Invention

Textile Treatment Agent

### 2. Claim(s)

[Claim 1] A textile treatment agent having as a main component water-dispersible resin composition prepared by compounding aqueous colloidal silica and/or a silane compound of specific structure depending on necessity to a water-dispersible silicon-modified vinyl polymer, which is produced by reaction of 100 parts by weight (converted to non-volatile content) of a water-dispersible vinyl-derived copolymer (I) obtained from 0.1 to 40 wt% of an organic silicon monomer (A) having at least one polymerizable unsaturated group and at least one hydrolyzable group directly bonded to a silicon atom in its molecule and organo-polysiloxane having a specific reaction group and 60 to 99.9 wt% of other polymerizable unsaturated monomers (B), and 0.2 to 1000 parts by weight of organo-polysiloxane (II) which has in its molecule a hydrogen atom directly bonded to at least one silicon atom and of which average compositional formula is expressed by  $\text{RaHbSiO} (4-a-b)/2$  [wherein R, a, b, and (a+b) represent a substituted or unsubstituted monovalent hydrocarbon group with 1 to 10 carbons,  $0.2 \leq a \leq 2.5$ ,  $0.0005 \leq b \leq 1.0$ , and  $0.3 \leq a+b \leq 3.0$ , respectively].

### 3. Detailed Description of the Invention]

#### [Industrial Application]

The present invention relates to a treatment agent for giving water resistance, water repellency and anti-melt property to fibers such as natural fiber, synthetic fiber, regenerated fiber, inorganic fiber and the like, or textile products. The said treatment agent according to the present invention is excellent in adhesive property for a variety of fibers and effectively used as a binder for various fibers or a coating agent for various textile products so that the fibers or textile products treated by the agent are given outstanding water resistance, water repellency and anti-melt property and etc for a long period of time. In addition, the textile treatment agent according to the present invention does not produce formalin when it is heated on the treatment and thus, it is characterized in that it does not cause any harm to human body.

### **[Prior Art and Problem(s) to be Solved by the Invention]**

Various fibers, and synthetic fibers, above all, polyester fiber, polyamide fiber, acryl fiber and the like are popularly used for clothing and various industrial materials. Products which are obtained from said synthetic fibers have a big drawback, however, that they are liable to be perforated with flame of match or cigarette or through contact with sparks in welding work, and a number of ways for improving their anti-melting property have been proposed so far. For example, Japanese Patent Publication No. S49-23279 proposes a method in which the treatment is done by heat-proof resin derived from isocyanuric acid derivative and Japanese Patent Publication No. S54-24040 proposes a method in which the treatment is done by a long chain polyamide compound and an organic phosphorous compound, but their anti-melting property and durability are not sufficient. Furthermore, Japanese Patent Publication No. S58-38551 proposes a method in which the treatment is done by a composition containing melamine derivative compound as a vital component and Japanese Patent Publication No. S52-17159 proposes a method in which the treatment is done by a composition composed of terminal silanolorgano-polysiloxane, methylhydrogen-polysiloxane and curing catalyst, but the former method has a problem that formalin is still existent in the textile product which was obtained by the treatment, while the latter method has drawbacks that the adhesive property of the textile treatment agent is insufficient, causing so-called shifting phenomena, and that the staining property of the product is decreased.

A variety of textile products subjected to water repellent treatment are now popularly used for sport clothing and leisure purposes. As to a method for giving water repellency to fibers, for example, Japanese Patent Publication No. S48-2718 proposes a method in which a composition containing chiefly methylhydrogen-polysiloxane and dimethyl-polysiloxane is treated, and Japanese Patent Publication No. S48-33438 proposes a method in which a composition containing methylolated melamine pre-condensate as a main component, but the former method has drawbacks that the shifting phenomena are caused with fibers and that the adhesive property of the textile treatment agent is insufficient, while the latter method has a problem that formalin is still existent in the fiber products after the treatment. Furthermore, it is proposed in Japanese Patent Publications No. S53-2998, S53-14672 and S53-15199 that the treatment is done by a high molecule having perfluoroalkyl radical, but the high molecule having perfluoroalkyl radical is rather expensive and thus, it is usual to use it at an amount as less as

possible wherein the product's water repellency can be obtained. As another problem, it is necessary to perform padding or coating process by using another high molecule in order to give waterproofness to the product, resulting in a complicated production process.

#### **[Means for Solving the Problem(s) and Effect]**

The inventor et al. have earnestly studied to obtain a textile treatment agent which is free from the problems as mentioned above, cheap and excellent in durability, found that a water-dispersible resin composition prepared by compounding aqueous colloidal silica and/or a silane compound of specific structure, if necessary, to a water-dispersible silicon-modified vinyl polymer, which is produced by the reaction of a water-dispersible vinyl-derived copolymer having a hydrolyzable group directly bonded to silicon atom and organo-polysiloxane having a specific reaction group, is excellent as a treatment agent for fibers to give them waterproofness, water repellency and anti-melt property, and completed the present invention.

Specifically, the present invention relates to a treatment agent having as a main component water-dispersible resin composition prepared by compounding aqueous colloidal silica and/or a silane compound of specific structure depending on necessity to a water-dispersible silicon-modified vinyl polymer, which is produced by reaction of 100 parts by weight (converted to non-volatile content) of a water-dispersible vinyl-derived copolymer (I) obtained from 0.1 to 40 wt% of an organic silicon monomer (A) having at least one polymerizable unsaturated group and at least one hydrolyzable group directly bonded to a silicon atom in its molecule and organo-polysiloxane having a specific reaction group and 60 to 99.9 wt% of other polymerizable unsaturated monomers (B), and 0.2 to 1000 parts by weight of organo-polysiloxane (II) which has in its molecule a hydrogen atom directly bonded to at least one silicon atom and of which average compositional formula is expressed by  $\text{RaHbSiO} \cdot (4-a-b)/2$  [wherein R, a, b, and (a+b) represent a substituted or unsubstituted monovalent hydrocarbon group with 1 to 10 carbons,  $0.2 \leq a \leq 2.5$ ,  $0.0005 \leq b \leq 1.0$ , and  $0.3 \leq a+b \leq 3.0$ , respectively].

The water-dispersible vinyl-derived copolymer (I) used to obtain the textile treatment agent according to the present invention is obtained from 0.1 to 40 wt% of an organic silicon monomer (A) which has at least one polymerizable unsaturated group and at least one hydrolyzable group directly bonded to a silicone atom in its molecule and 60 to 99.9 wt% of other polymerizable unsaturated monomers (B).

Specific examples of the organic silicon monomer (A) include, for example, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltributoxysilane, allyltrimethoxysilane, allyltriethoxysilane, trimethoxysilyl-propylallylamine,  $\gamma$ -(meth)acryloxypropyl-trimethoxysilane,  $\gamma$ -(meth)acryloxypropyl-methyldimethoxysilane,  $\gamma$ -(meth)acryloxypropyl-triethoxysilane, N-vinylbenzyl- $\gamma$ -aminopropyl-trimethoxysilane, 2-styrylethyl-trimethoxysilane, vinyltriacetoxysilane, vinyltrichlorosilane etc., and one or more than 2 kinds of mixtures to be selected from the said groups can be used. The organic silicon monomer (A) in the present invention is an indispensable component for the reaction between the cross-linking reactive and water-dispersible vinyl-derived copolymer (I) and the organo-polysiloxane (II) of the textile treatment agent obtained, and it is required to use it at an amount of 0.1 to 40 wt% among all the monomers. When its ratio is less than 0.1 wt%, it will be caused that the cross-linking reactivity of the textile treatment agent obtained is decreased so that its anti-melt, water resistant and solvent resistant properties will be lowered, and its durability such as water repellency and the like will be also lowered due to unsuccessful reaction between the water-dispersible vinyl-derived copolymer (I) and the organo-polysiloxane (II). In the case that its excessive amount more than 40 wt% is used, an enhanced performance may not be expected and on the contrary, it is not preferable because the costs will be increased and the stability of the textile treatment agent obtained is rather lowered.

Specific examples of the other polymerizable unsaturated monomers (B) to be used in the present invention include, for example, unsaturated monobasic acids such as acrylic acid, methacrylic acid, crotonic acid etc, unsaturated dibasic acids such as maleic acid, fumaric acid, itaconic acid etc, monoester compounds of alkyl alcohol with 1-17 carbons and unsaturated dibasic acids, unsaturated carboxylic acids such as monoester compounds between monoethers of dihydric alcohols like ethylene glycol, diethylene glycol, propylene glycol etc and lower monohydric alcohols like methyl alcohol, ethyl alcohol, butyl alcohol etc and unsaturated dibasic acids; (meth)acrylic acid alkyl esters such as (meth)acrylic acid methyl, ethyl, propyl, butyl, isobutyl, octyl, 2-ethylhexyl or cyclohexyl ester; unsaturated alcohols such as (meth)allyl alcohol, croton alcohol etc; olefin hydrocarbons such as ethylene, propylene, butylene etc; vinyl aromatic hydrocarbons such as styrene, chlorostyrene, vinyl toluene etc; vinyl halides such as vinyl fluoride, vinyl chloride, vinyl bromide etc; vinylidene halides such as vinylidene fluoride, vinylidene chloride etc; unsaturated nitriles such as (meth)acrylonitrile, croton nitrile etc; monovalent carboxylic acid vinyl-esters such as acetic acid, propionic acid etc; monohydric

alcohol vinyl-ethers such as methyl alcohol, ethyl alcohol, propyl alcohol etc; unsaturated aldehydes such as (meth)acrolein, croton-aldehyde etc; amino group-containing (meth)acrylates such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate etc; unsaturated acid amides such as (meth)acrylamide, diacetone (meth)acrylamide etc; diene hydrocarbons such as butadiene, isoprene etc; alkylene glycol monomethacrylic acid esters such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate etc; unsaturated glycidyl esters such as glycidyl (meth)acrylate or the like, and one or more than 2 kinds of mixtures to be selected from the said groups can be used at an amount of 60 to 99.9 wt% among all the monomers.

When the other polymerizable unsaturated monomers (B) are used, the combination of the monomers and their amounts to be used are not particularly limited, but it is preferable in terms of the stability of the textile treatment agent obtained and its adhesion property to various fibers to use the unsaturated carbon acids at a ratio of 0.1 to 20 wt% among all the monomers. When the ratio of the unsaturated carbon acids is less than 0.1 wt%, the adhesion property of the textile treatment agent obtained to various fibers will be lowered and its stability will be lost. On the contrary, the use of a lot of the unsaturated carbon acids over 20 wt% may occasionally decrease the water resistance of the textile treatment agent obtained.

The water-dispersible vinyl-derived copolymer (I) is produced by emulsion polymerization of the organic silicon monomer (A) and other polymerizable unsaturated monomers (B) in an aqueous medium. As to the textile treatment agent, it is not necessarily to use an aqueous medium, but it is preferable not to use an organic solvent from the view points of resources saving and working hygiene. Accordingly, it is possible in the present invention to use a method for obtaining the water-dispersible vinyl-derived copolymer (I) in which following the polymerization of the said monomers in an organic solvent the resulting compound is dispersed in water, but it is the best way from the view points of avoiding the risk of fire, improving the working environment and the simplified production process to carry out the emulsion polymerization in an aqueous medium. The emulsion polymerization can be conducted in the known methods by using known polymerization initiator, emulsifier and various additives if necessary.

The water-dispersible silicon-modified vinyl polymer which is a vital component of the textile treatment agent according to the present invention is produced by reacting said water-dispersible vinyl-derived copolymer (I) with the

organo-polysiloxane (II) at a ratio of 100 parts by weight (converted to non-volatile content) of the former to 0.2 to 1000 parts by weight of the latter. When the ratio of the organo-polysiloxane (II) is less than 0.2 parts by weight, the reaction with the water-dispersible vinyl-derived copolymer (I) cannot reach a substantially effective volume, resulting in insufficient water repellency and anti-melt property. In the case that its excessive amount more than 1000 parts by weight is used, an enhanced performance in proportion to the added amount may not be expected and on the contrary, it is not preferable because the costs will be increased and the stability of the textile treatment agent obtained is rather lowered.

The organo-polysiloxane (II) to be used in the present invention is an organo-polysiloxane which has in its molecule a hydrogen atom directly bonded to at least one silicon atom and of which average compositional formula is expressed by  $\text{RaHbSiO} (4-a-b)/2$  [where R, a, b, and (a+b) represent a substituted or unsubstituted monovalent hydrocarbon group with 1 to 10 carbons,  $0.2 \leq a \leq 2.5$ ,  $0.0005 \leq b \leq 1.0$ , and  $0.3 \leq a+b \leq 3.0$ , respectively.] The hydrogen atom directly bonded to a silicone atom is indispensable for the reaction with a silicon-derived hydrolyzable group contained in the water-dispersible vinyl-derived copolymer (I) and it is necessary that at least one in a molecule of the organo-polysiloxane (II) or preferably more than one per 100 silicon atoms is contained. On the other hand, when the number of hydrogen atoms directly bonded to silicone atoms is over 100 per 100 silicon atoms, coagulation is liable to happen during the reaction with the water-dispersible vinyl-derived copolymer (I) and it is thus not preferable. The number of silicon atoms contained in a molecule is not particularly limited, but 4 or more and 2000 or less is preferably appropriate. When there are 4 atoms or less, the feature of silicon can be hardly exhibited, and when there are 2001 atoms or more, drawbacks such as lowered reactivity or events of separation and coagulation will be shown. The organo-polysiloxane (II) can be used in the original form of liquid or in a dispersed emulsion form in an aqueous medium under the presence of emulsifier.

The reaction between the water-dispersible vinyl-derived copolymer (I) and the organo-polysiloxane (II) is carried out, for example, by mixing the water-dispersible vinyl-derived copolymer (I) obtained by said polymerization with the organo-polysiloxane (II), or by polymerization of a mixture of the monomers comprising of said organic silicon monomer (A) and other polymerizable unsaturated monomers (B) under the presence of the organo-polysiloxane (II). To mix the organo-polysiloxane (II) in the latter method, a variety of methods may be

employed;

(a) Polymerization through dropping down of said mixture of monomers into a medium containing the organo-polysiloxane (II)

(b) Polymerization through dropping down of the premix of the organo-polysiloxane (II) and said mixture of monomers into a medium

(c) Polymerization through separate dropping down of the organo-polysiloxane (II) and said mixture of monomers into a medium:

The water-dispersible silicon-modified vinyl polymer is produced by a reaction between the water-dispersible vinyl-derived copolymer (I) and the organo-polysiloxane (II) at the temperatures from room temperature to 100 degrees C, preferably from 50 to 85 degrees C, whereby the hydrogen produced during the reaction is being cleared from the process, and it is preferable for shortening the reaction period to use a proper reaction catalyst. As such a reaction catalyst, those are useful which are commonly used in the condensation reaction between the silicon-derived hydrolyzable group and the hydrogen atom directly bonded to the silicon atom; for example, carbon acid metal salts such as dibutyltin diacetate, dibutyltin dilaurate, tin acetate, lead naphthenate, zinc caprylate, zirconium acetate, iron 2-ethylhexanoate, cobalt naphthenate etc; titanate acid esters such as titanate acid tetrabutyl ester, titanate acid tetranonyl ester and its multimer etc; basic substances such as lithium hydroxide, sodium hydroxide, potassium hydroxide, sodium methylate, ammonia, triethylamine, triethanolamine, and the like, and one or more than 2 kinds of mixtures to be selected from the said groups can be used. A preferable way of using the catalyst is such that a metal salt such as dibutyltin diacetate, zinc caprylate, iron 2-ethylhexanoate etc and a basic substance such as sodium hydroxide, ammonia, triethylamine etc are used together. The amount of the reaction catalyst to be used is not particularly limited, but it may be used as a guiding value at an amount of 0.05 to 10 parts by weight relative to 100 parts by weight of non-volatile content of the water-dispersible silicon-modified vinyl polymer. The reaction catalyst may be used before or after the water-dispersible vinyl-derived copolymer (I) and the organo-polysiloxane (II) are mixed.

It has been already explained that a preferable polymerization method is the emulsion polymerization, wherein the reaction between the water-dispersible vinyl-derived copolymer (I) and the organo-polysiloxane (II) may be carried out by mixing of the water-dispersible vinyl-derived copolymer (I) and the organo-polysiloxane (II) after the emulsion polymerization as mentioned above, or by the emulsion polymerization of the water-dispersible vinyl-derived copolymer (I)



in the presence of the organo-polysiloxane (II). In the former method, the components of the organo-polysiloxane (II) are liable to localize and thus, more components of the organo-polysiloxane can be concentrated onto its surface when it is formed as a film so that it has a feature that it can be effectively utilized at a small amount. In the latter method for the emulsion polymerization, any emulsion polymerization methods which have been known so far can be applied as well as a method in which the organo-polysiloxane (II) is not co-existent.

With regard to the textile treatment agent of the present invention, the said water-dispersible silicon-modified vinyl polymer can be compounded with a silane compound having a hydrolyzable group directly bonded to aqueous colloidal silica and silicon atom, if necessary. Compounding of the aqueous colloidal silica and the silane compound has an effect that adhesion, water resistance, solvent resistance and etc particularly relative to inorganic fibers.

The aqueous colloidal silica which is used in the present invention depending on necessity is a so-called condensate of silicic acid and preferable ones has particle size of 5 to 100 microns and most preferably 7 to 50 microns. Usually available ones in the form of aqueous dispersible solution can be directly used. Specific examples of such aqueous colloidal silica include, for instance as commercially available ones, "SNOWTEX O", "SNOWTEX N", "SNOWTEX NCS", "SNOWTEX 20" and "SNOWTEX C" (made by Nissan Chemical Industries, Ltd.) and "Cataloid SN" and "Cataloid Si-500" (made by Shokubai Kasei Kogyo K. K.) and surface-treated colloidal silica such as "Cataloid SA" treated with aluminic acid (made by Shokubai Kasei Kogyo K. K.), and one or more than 2 kinds of mixtures to be selected from the said groups can be used.

As a method for compounding the water-dispersible silicon-modified vinyl polymer with the aqueous colloidal silica, it is possible to simply mix the water-dispersible silicon-modified vinyl polymer with the aqueous colloidal silica, or to carry out an emulsion polymerization of the water-dispersible vinyl-derived copolymer (I) in the presence of the aqueous colloidal silica. In the latter method, the known methods such as the monomer dropping down method, pre-emulsion method, a combination thereof and the like can be used. For example, methods in which polymerization is carried out by dropping down of a monomer mixture into an aqueous medium containing aqueous colloidal silica, or by dropping down of a premix of aqueous colloidal silica and a monomer mixture, or by separately dropping down of a premix of aqueous colloidal silica and a monomer mixture or the like can be employed. In the emulsion polymerization under the presence of aqueous

colloidal silica, any known emulsifiers and polymerization catalysts can be used, and usual additives can be freely used, depending on necessity. Through the emulsion polymerization of the water-dispersible vinyl-derived copolymer (I) under the presence of aqueous colloidal silica the cross-linking degree of the textile treatment agent occasionally may be further improved in comparison with simple mixing of the water-dispersible silicon-modified vinyl polymer and the aqueous colloidal silica.

When the aqueous colloidal silica is used in the present invention, it is preferable that the aqueous colloidal silica is used at an amount of 200 parts by weight (converted to SiO<sub>2</sub> content) or less relative to 100 parts by weight (converted to non-volatile content) of the water-dispersible silicon-modified vinyl polymer. Even if a lot of its amount exceeding 200 parts by weight is used, the improved performance in proportion to the amount used cannot be expected, but on the contrary, drawbacks such as unstable textile treatment agent, increased costs and the like will be unfavorably caused.

The water dispersible resin composition in which the water-dispersible silicon-modified vinyl polymer obtained and the aqueous colloidal silica depending on necessity are compounded can exhibit an excellent performance as the textile treatment agent when it is solely used, but it is possible to further enhance its adhesion, water resistance and solvent resistance to various fibers by using the said silane compound together. In addition, the silane compound has another effect.

That is, it may occasionally happen that the water dispersible resin composition in which the water-dispersible silicon-modified vinyl polymer obtained and the aqueous colloidal silica depending on necessity are compounded does not keep its initial adhesion to fibers when it is used as textile treatment agent after storage for a certain period, for example, one year or longer. In that case, its initial adhesion to fibers can be recovered by compounding the silane compound into the polymer or composition after storage for a certain period.

Specific examples of the silane compound which can be used in the present invention include in addition to compounds to be used as the said organic silica monomer (A), for example, aminoalkylalkoxysilanes such as aminomethyltriethoxysilane, N-β-aminoethylaminomethyltrimethoxysilane, γ-aminopropyltrimethoxysilane, N-β-aminoethyl-γ-aminopropylmethyldimethoxysilane etc; epoxyalkylalkoxysilanes such as γ-glycidoxypropyltrimethoxysilane, γ-glycidoxypropylmethyldimethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane etc; mercaptoalkylalkoxysilanes such as γ-ethylmethyldimethoxysilane, γ-mercaptopropyltrimethoxysilane etc; tetraalkoxysilanes such as

tetramethoxysilane, tetraethoxysilane, tetrapropoxysilane, tetrabutoxysilane etc; alkyltrialkoxysilanes such as methyltrimethoxysilane, methyltriethoxysilane, methyltrimethoxyethoxysilane etc; dialkyldialkoxysilanes such as dimethyldimethoxysilane, dimethyldiethoxysilane etc; alkylalkoxysilane halides such as  $\gamma$ -chloropropyltrimethoxysilane, 3,3,3-trichloropropyltrimethoxysilane etc; alkylacyloxysilanes such as methyltriacetoxysilane, dimethyldiacetoxysilane etc; hydrosilane compounds such as trimethoxysilane, triethoxysilane etc, and the like, and one or more than 2 kinds of mixtures to be selected from the said groups can be used.

In order to have its desired effect sufficiently exhibit and to keep the costs of the textile treatment agent in a reasonable range, it is preferable to use these silane compounds at an amount of 20 parts by weight relative to 100 parts by weight (converted to non-volatile content) of the water-dispersible silicon-modified vinyl polymer.

The water dispersible resin composition in which the water-dispersible silicon-modified vinyl polymer obtained and the aqueous colloidal silica depending on necessity are compounded can be solely used as the textile treatment agent, but it is possible to further add thereto a variety of known viscosity modifier, water repellent, cross-linker, foaming agent, inorganic filler and the like, and it can be used through mechanical foaming process or diluting process.

#### [Effect of the Invention]

The water-dispersible resin composition according to the present invention has a water dispersible resin composition as its vital component prepared by compounding aqueous colloidal silica and/or a silane compound of specific structure depending on necessity to a water-dispersible silicon-modified vinyl polymer, which is produced by reaction of a water-dispersible vinyl-derived copolymer (I) obtained from an organic silicon monomer (A) and other polymerizable unsaturated monomers (B) with organo-polysiloxane (II) having a specific reaction group and thus, it can give excellent waterproofness, water repellency and anti-melt property to various fibers when they are treated with it, and its performance can be kept in a long period of time. Furthermore, it has also an excellent feature from the view point of working hygiene, because it does not produce formalin but only water is volatilized when it is heated. Therefore, the treatment agent according to the present invention can be favorably used as a binder for a variety of fibers such as , for example, natural fiber, synthetic fiber, regenerated fiber, inorganic fiber and the like, as well as a binder or coating agent for various textile products.

### <Working Examples>

The present invention is illustrated in detail but not limited by the following Working Examples. In addition, all the terms "part(s)" and "%" stand for "part(s) by weight" and "wt %" respectively in Reference Examples, Comparative Reference Examples, Working Examples and Comparative Examples. Moreover, the following are descriptions of the organopolysiloxanes used in these examples.

#### Organopolysiloxane (1)

Average compositional formula  $(\text{CH}_3)_{1.15}\text{H}_{0.95}\text{SiO}_{0.95}$

Average molecular weight 2500

#### Organopolysiloxane (2)

Average compositional formula  $(\text{CH}_3)_{0.9}(\text{C}_6\text{H}_5)_{1.0}\text{H}_{0.3}\text{SiO}_{0.9}$

Average molecular weight 1500

#### Organopolysiloxane (3)

Average compositional formula  $(\text{CH}_3)_{1.9}\text{H}_{0.1}\text{SiO}$

Average molecular weight 30000

#### Aqueous emulsion of organopolysiloxane

Methylhydrogenpolysiloxane emulsion (Product name: Polon MR, manufactured by Shin-Etsu Chemical Co., Ltd., Active ingredient: 60 %)

### Reference Example 1

Deionized water (154 parts), sodium lauryl sulfate (1 part), polyoxyethyleneoleic acid ester (3 parts, HLB = 9) and potassium persulfate (0.4 parts) were put in a flask equipped with a dropping funnel, stirrer, tube for introducing inert gas, thermometer and reflux/cooling tube, and the mixture was heated to 75 °C and stirred while gently blowing nitrogen gas therein, in order to produce a homogeneous aqueous solution. Then a monomer mixture of vinyltrimethoxysilane (5 parts), acrylic acid (3 parts), acrylonitrile (10 parts) and butyl acrylate (82 parts) was dropped through the dropping funnel for 2 hours. Subsequently, the mixture was stirred continuously for an hour while maintaining the temperature at 75 °C and cooled down to room temperature, followed by adding a 28 %-aqueous ammonia for the sake of adjusting pH to approximately 8, in order to obtain a water-dispersible vinyl copolymer (1) having a non-volatile content of approximately 40 %.

### Reference Examples 2-4

By following the same procedure as the above Reference Example 1 except for

using the monomer mixtures, emulsifiers, polymerization catalysts, water and neutralizers shown in Table 1, water-dispersible vinyl copolymers (2)-(4) were obtained. Their properties are summarized in Table 1.

#### **Comparative Reference Example 1**

By following the same procedure as the above Reference Example 1 except for using the monomer mixture shown in Table 1, which was outside the scope of the present invention, a water-dispersible vinyl copolymer (5) was obtained. Its properties are shown in Table 1.

Table 1

	Reference Example 2	Reference Example 3	Reference Example 4	Comparative Reference Example 1
The obtained water-dispersible vinyl copolymer	(2)	(3)	(4)	(5)
Monomer mixture (parts)	3.0	10.0	2-Styrylethyltrimethoxysilane	3.0
	Methacryloxypropyltrimethoxysilane			Acrylic acid
	10.0	1.0	Methyl methacrylate	10.0
	Hydroxyethyl acrylate			Acrylonitrile
	3.0	20.0	Vinyl acetate	87.0
Emulsifier (parts)	84.0	69.0		
	Ethyl acrylate			Butyl acrylate
	1.0	2.0	Polyoxyethylene nonylphenyl ether ammonium sulfate	1.0
	Sodium dodecylbenzene sulphonate			Sodium lauryl sulfate
	8.0	6.0	Polyoxyethylene oleyl ether (HLB = 12)	3.0
Polymerization catalyst (parts)	0.5	0.1 / 0.1	Ammonium persulfate / Sodium hydrogen sulfite	0.4
	Ammonium persulfate			Potassium persulfate
	110	150	200	154
	28 % Aqueous ammonia	28 % Aqueous ammonia	—	28 % Aqueous ammonia
	6.0	6.0	2.5	8.0
pH				
Nonvolatile content (%)	50	40	30	40

### Working Example 1

The water-dispersible vinyl copolymer (1) (258 parts) obtained in Reference Example 1 and dibutyltin diacetate (0.3 parts) were put in the same flask as that used in Reference Example 1, and the mixture was heated to 75 °C while stirring. Then the organopolysiloxane (1) (3 parts) represented by the average compositional formula  $(\text{CH}_3)_{1.15}\text{H}_{0.95}\text{SiO}_{0.95}$  having an average molecular weight of 2500 was dropped through the dropping funnel for 30 minutes. Subsequently, the mixture was stirred continuously for 2 hours while maintaining the temperature at 75 °C and cooled down to room temperature, in order to obtain a textile treating agent (1) consisting of a water-dispersible silicon-modified vinyl polymer.

### Working Examples 2-4

By following the same procedure as the above Working Example 1 except for using the water-dispersible vinyl copolymers, organopolysiloxanes, reaction catalysts and reaction conditions shown in Table 2, textile treating agents (2)-(4) were obtained.

Table 2

	Working Example 2	Working Example 3	Working Example 4
The obtained textile treating agent	(2)	(3)	(4)
Composition (parts)	Water-dispersible vinyl copolymer (2)	Water-dispersible vinyl copolymer (3)	Water-dispersible vinyl copolymer (4)
	219	258	310
	Dibutyltin dimaleate	Zinc caprylate	Iron 2-ethylhexanoate
	0.6	2.0	3.0
	Organopolysiloxane (1)	5 %-Aqueous solution of sodium hydroxide	28 %-Aqueous ammonia
	6.0	10.0	6.0
		Organopolysiloxane (2)	Organopolysiloxane (3)
		20.0	15.0
Reaction temperature	75 °C	60 °C	80 °C
Reaction time	2 hours	4 hours	3 hours



#### Working Example 5

Deionized water (152 parts), sodium lauryl sulfate (1 part), polyoxyethyleneoleic acid ester (3 parts, HLB = 9), an aqueous emulsion of organopolysiloxane (5 parts, Active ingredient: 60 %), dibutyltin dilaurate (0.3 parts) and potassium persulfate (0.4 parts) were put in the same flask as that used in Reference Example 1, and the mixture was heated to 75 °C and stirred while gently blowing nitrogen gas therein, in order to produce a homogeneous aqueous solution. Then a monomer mixture of vinyltrimethoxysilane (5 parts), acrylic acid (3 parts), acrylonitrile (10 parts) and butyl acrylate (82 parts) was dropped through the dropping funnel for 2 hours. Subsequently, the mixture was stirred continuously for 2 hours while maintaining the temperature at 75 °C and cooled down to room temperature, followed by adding a 28 %-aqueous ammonia for the sake of adjusting pH to approximately 8, in order to obtain a textile treating agent (5) consisting of a water-dispersible silicon-modified vinyl polymer.

#### Working Example 6

Deionized water (110 parts), sodium dodecylbenzene sulphonate (1.0 part), sorbitan monostearate (8.0 parts, HLB = 4.7), titanate acid tetrabutyl ester (0.6 parts), aqueous colloidal silica "SNOWTEX O" (manufactured by Nissan Chemical Industries, Ltd., Particle size: 10-20  $\mu\text{m}$ ,  $\text{SiO}_2$  content: 20 %) (50 parts) and ammonium persulfate (0.5 parts) were put in the same flask as that used in Reference Example 1, and the mixture was heated to 75 °C and stirred while gently blowing nitrogen gas therein, in order to produce a homogeneous aqueous solution. Then a mixture of  $\gamma$ -methacryloxypropyltrimethoxysilane (3 parts), methacrylic acid (2 parts), hydroxyethyl acrylate (10 parts), ethyl acrylate (85 parts) and the organopolysiloxane (2) (6 parts) was dropped through the dropping funnel for 2 hours. Subsequently, the mixture was stirred continuously for 2 hours while maintaining the temperature at 75 °C and cooled down to room temperature, in order to obtain a textile treating agent (6).

#### Working Example 7

Deionized water (154 parts), sodium lauryl sulfate (1 part), polyoxyethyleneoleic acid ester (3 parts, HLB = 9), aqueous colloidal silica "SNOWTEX C" (manufactured by Nissan Chemical Industries, Ltd., Particle size: 10-20  $\mu\text{m}$ ,  $\text{SiO}_2$  content: 20 %) (60 parts), an aqueous emulsion of organopolysiloxane (5 parts, Active ingredient: 60 %) and potassium persulfate (0.5 parts) were put in the same flask as that used in Reference Example 1, and the mixture was heated to 80 °C and stirred while gently blowing nitrogen gas therein, in order to produce a homogeneous aqueous solution. Then a monomer mixture of vinyltriethoxysilane (3 parts), acrylic acid (1 part), methyl methacrylate (10 parts), ethyl acrylate (20 parts) and butyl acrylate (66 parts) was dropped through the dropping funnel

for 3 hours. Subsequently, dibutyltin dilaurate (0.8 parts) was added thereto, and the mixture was stirred continuously for 2 hours while maintaining the temperature at 80 °C and cooled down, followed by adding a 28 %-aqueous ammonia for the sake of adjusting pH to approximately 7 as well as  $\gamma$ -glycidoxypyrroltrimethoxysilane (3 parts), in order to obtain a textile treating agent (7).

### **Working Example 8**

A performance test was conducted for each of the textile treating agents (1)-(7) obtained in Working Examples 1-7, assuming that they were to be used as an agent for treating organic or inorganic fiber. The results are shown in Table 3. Additionally, the performance test was carried out according to the following procedures.

#### **① Treatment of organic fiber**

##### Treatment conditions

A 28 %- aqueous ammonia was added to the textile treating agent so that the viscosity was adjusted to 25000 cps, and the mixture was applied uniformly to polyester twill 9A to a coating weight of 10 g/m<sup>2</sup> by means of a doctor knife, followed by a 5 minute-drying by heating at 100 °C, in order to prepare a processed fabric to be used for the test on organic fiber.

##### Water repellency

According to the spray method of JIS L 1004, the processed fabric was tested for the water repellency at the beginning and after washing.

##### Waterproofness

According to the water pressure method of JIS L 1004, the processed fabric was tested for the anti-water pressure characteristic at the beginning and after washing.

##### Anti-melt properties

The processed fabric was set in an embroidery frame 10 cm in diameter, and a laterally supported lit cigarette (Seven Stars) was placed thereon, so that the live side touched the processed fabric perpendicularly, in order to measure the time until the cigarette fell owing to a hole made by melting of the processed fabric.

##### Resistance to washing with water

The processed fabric was washed with a detergent solution (Super ZAB, 0.5 g/l) at 40 °C for 15 minutes by using a domestic electric washing machine, and then rinsed with running water at 40 °C for 5 minutes, followed by a 24-hour drying at ordinary temperature. Defining this procedure as 1 cycle, the processed fabric was tested for the aforementioned water repellency, waterproofness and anti-melting properties after completion of 5 cycles.

#### Dry-cleaning resistance

The processed fabric was cleaned with a perchloroethylene solution of Marseilles soap (0.5 g/l) by using the Dry Cleaning Tester at ordinary temperature for 2 hours, followed by a 24-hour drying at ordinary temperature. The obtained processed fabric was tested for the aforementioned water repellency, waterproofness and anti-melting properties.

#### ② Treatment of inorganic fiber

##### Treatment conditions

A felted fiberglass mat was impregnated with a binder, which was prepared by mixing the textile treating agent and aqueous ammonia so that pH was adjusted to approximately 10.5 and by diluting the mixture with water so that the non-volatile content was 8 %; and after attaining the prescribed adhesion volume, the mat was dried at 200 °C for 2 minutes, in order to obtain a fiberglass mat to be tested, in which the adhesion volume of the binder (non-volatile content) was 15 %.

##### Water repellency

According to the spray method of JIS L 1004, the fiberglass mat was tested for the water repellency at the beginning and after washing.

##### Hardness

A test strip of 1 x 12 cm was cut off from the fiberglass mat and movably supported at the points located 1 cm from both ends, while putting a 2 g-weight in the center thereof, in order to determine the distance moved down by the center part (in mm). The distance becomes shorter in proportion to the goodness of the adhesive properties of the binder to the glass fiber.

##### Water resistance

A test strip of 1 x 12 cm was cut off from the fiberglass mat and soaked in deionized water for 24 hours; and then it was tested in a similar manner to the aforementioned hardness test immediately after being raised.

#### **Comparative Examples 1-4**

The water-dispersible vinyl copolymers (1)-(4) obtained in Reference Examples 1-4 were tested in a similar manner to Working Example 8, without denaturing them by using the organopolysiloxanes. The results are shown in Table 3.

#### **Comparative Example 5**

The water-dispersible vinyl copolymer (5) (258 parts) obtained in Comparative Reference Example 1 and dibutyltin diacetate (0.3 parts) were put in the same flask as that used in Reference Example 1, and the mixture was heated to 75 °C while stirring. Then the organopolysiloxane (1) (3 parts) represented by the average compositional formula  $(\text{CH}_3)_{1.15}\text{H}_{0.95}\text{SiO}_{0.95}$  having an average molecular weight of 2500 was dropped

through the dropping funnel for 30 minutes. Subsequently, the mixture was stirred continuously for 2 hours while maintaining the temperature at 75 °C and cooled down, in order to obtain a treating agent for comparison (1). This treating agent was tested in a similar manner to Working Example 8. The results are shown in Table 3.

#### **Comparative Example 6**

By following the same procedure as the above Working Example 1 except for changing the volume of the organopolysiloxane (1) to 0.1 parts, a treating agent for comparison (2) was obtained, in which the volume of the organopolysiloxane was outside the scope of the present invention. This treating agent was tested in a similar manner to Working Example 8. The results are shown in Table 3.

#### **Comparative Example 7**

By following the same procedure as the above Working Example 1 except for changing the volume of the organopolysiloxane (1) to 2000 parts, a treating agent for comparison (3) was obtained, in which the volume of the organopolysiloxane was outside the scope of the present invention. This treating agent was tested in a similar manner to Working Example 8. The results are shown in Table 3.

Table 3

	Agent used for treating textile	Treatment of organic fiber									Treatment of inorganic fiber		
		Water repellency			Waterproofness (mmH <sub>2</sub> O)			Anti-melting properties (sec.)			Water repellency	Hardness (mm)	Water resistance (mm)
		At beginning	After washing with water	After dry cleaning	At the beginning	After washing with water	After dry cleaning	At the beginning	After washing with water	After dry cleaning			
Working Example 8	Textile treating agent (1)	70	70	70	1100	1000	1000	120	110	100	70	8	8
	Textile treating agent (2)	80	80	80	1100	1000	1000	160	120	120	70	7	7
	Textile treating agent (3)	90	90	90	1200	1100	1000	160	140	130	80	6	6
	Textile treating agent (4)	80	80	80	1300	1200	1000	160	140	120	70	6	7
	Textile treating agent (5)	90	90	90	1100	1000	1000	120	110	100	80	8	8
	Textile treating agent (6)	90	90	90	1200	1100	1000	130	110	110	80	8	9
	Textile treating agent (7)	90	90	90	1100	1000	1000	160	150	130	80	6	6
Comparative Example 1	Water-dispersible vinyl copolymer (1)	0	0	0	750	500	500	20	10	7	0	8	10
Comparative Example 2	Water-dispersible vinyl copolymer (2)	0	0	0	770	500	450	35	22	10	0	7	8
Comparative Example 3	Water-dispersible vinyl copolymer (3)	50	50	50	700	450	400	12	7	4	50	6	8

Comparative Example 4	Water-dispersible vinyl copolymer (4)	0	0	0	780	600	400	22	14	6	0	12	18
Comparative Example 5	Treating agent for comparison (1)	70	50	0	1000	700	500	22	10	8	50	12	18
Comparative Example 6	Treating agent for comparison (2)	0	0	0	780	750	700	40	20	18	0	8	12
Comparative Example 7	Treating agent for comparison (3)	90	50	0	970	700	450	120	20	18	80	18	22